TIME OF REMEDIATION ESTIMATES

Enhanced Bioremediation at ST012

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Summary

The attached memorandum describes a screening level evaluation of enhanced bioremediation (EBR) applied to NAPL (nonaqueous hydrocarbon liquid) source zone targets at ST012. The purpose of the effort is to estimate timeframes for completing the remediation using a volume-averaged "box model" which is based on a time-dependent hydrocarbon mass balance for the NAPL source zones and the aqueous-phase pore-water and soil (sorbed) phases in the porous media. Contaminants dissolve out of the NAPL into surrounding groundwater and then undergo biological degradation. Remediation is complete when contaminant fractions in the NAPL are reduced to levels that no longer impact groundwater above cleanup goals. The duration to attain this goal is known as the time of remediation (TOR). Sulfate reduction was selected as the bioremediation process to be enhanced with the underlying assumption that the addition of sulfate will accelerate the degradation of hydrocarbon contaminants by serving as an electron acceptor for anaerobic microbial respiration. The evaluation assumes a range of initial conditions (e.g., NAPL volume, hydrocarbon composition in the NAPL, sulfate concentration) and input-parameter values (e.g., hydrocarbon utilization rate by sulfate-reducing bacteria, rate of NAPL dissolution into groundwater, soil porosity).

Detailed numerical calculations for monitored natural attenuation before and following a hypothetical application of SEE were performed previously using the SEAM3D Model as reported in Appendix M of the TEE Pilot Test Evaluation Report (BEM, 2011). Those calculations were very complex; however, model parameters were calibrated to field data. Depletion of individual NAPL source zones can be estimated to the same order-of-magnitude as the SEAM3D modeling using volume-averaged mass balances (i.e., box models) that include the same mechanisms of remediation averaged over each target soil volume. Details of the volume-averaged box model are provided in Appendix B of the memorandum. The box model includes mass transfer limitations on the dissolution of hydrocarbon components from the NAPL. It is very important to note that the biodegradation model used by AMEC to estimate TOR values for EBR did not include these important mass-transfer limitations; the AMEC model assumes that an equilibrium exists between the pore-water and NAPL hydrocarbon concentrations (i.e., the mass-transfer rate is very large relative to biodegradation rates). As discussed below, site-specific field mass transfer tests have been performed which demonstrate that hydrocarbon dissolution from NAPL is highly rate-dependent, which is also consistent with numerous other field and laboratory studies. The calculations using the volume-averaged model show that rate-limited NAPL dissolution ~~will generally~~ can cause significantly increased remediation time frames. Biodegradation in the volume-averaged model was simulated with two different

Commented [DE1]: Maybe this is obvious, but should you also state that Amec's NAPL mass estimates were used in these calculations?

Commented [DJC2]: I'll let Bo address Eva's comment approaches to illustrate the impacts of modeling assumptions on TOR estimates: first-order biodegradation and a dual-Monod kinetics (hydrocarbon and sulfate concentrations) model that incorporated biomass growth. The first-order biodegradation model assumes that biodegradation rates only depend on (are directly proportional to) the product of dissolved-phase hydrocarbon (e.g., benzene) concentrations in groundwater (the electron donor, or food source) and a simple empirical degradation rate constant (inversely proportional to a degradation half-life) that does not change during the entire EBR simulation. The first-order model ignores several potentially significant factors and assumes that hydrocarbon biodegradation rates are not limited by the availability of either sulfate-reducing bacteria (SRB; biomass is assumed constant and not limiting) or the sulfate (electron acceptor) used for anaerobic respiration. The first-order model also ignores the fact that the vast majority of the hydrocarbon contaminant is present as a nonaqeous phase liquid (NAPL) and that slow dissolution of hydrocarbons from the NAPL is generally a rate-limiting step in the biodegradation process, which primarily occurs in the aqueous phase. In contrast, the more-comprehensive Monod kinetics model incorporates the effects of transient biomass (degradation is proportional to biomass concentrations), sulfate (degradation rates reduce at low sulfate levels), and hydrocarbon concentrations on biodegradation rates. The volume-averaged model with Monod kinetics ~~model~~ also incorporates the important rate-limited mass transfer mechanism for NAPL dissolution.

Times of remediation (TOR) for untreated NAPL targets using EBR were first calculated assuming a simple first-order biodegradation model, very high NAPL dissolution (i.e., equilbrium between NAPL and aqueous-phase hydrocarbon concentrations), and the highest first-order decay constant for degradation (0.0125 d^{-1}) suggested by AMEC for the Lower Saturated Zone (LSZ). These calculations are presented in Section 4 of the Memorandum. Note that the first-order rate constant used by AMEC for EBR modeling of the Upper Water Bearing Zone (UWBZ) was a factor of 20 lower than the LSZ value (RD-RAWP report, Table E-4.11). Further, these first-order rates are actually maximum hydrocarbon utilization rates that assume consistently high biomass concentrations that are not limited by either sulfate (anaerobic respiration) or hydrocarbon (electron donor) availability. Moreover, very little site data exist to support the selection of a generic, first-order decay rate for a specific hydrogeologic unit, and biodegradation rates ~~values~~ are not expected to remain constant over time at such high values ~~rates~~. Nevertheless, using the rate constant cited by AMEC for the LSZ (0.0125 d^{-1}) in Work Plan submittals, the calculated TOR ranged from 10 to 20 years in the UWBZ and 10 to 30 years in the LSZ (Memorandum Table 6). This biodegradation rate constant (55-day half-life) is very high (consistent with more favorable aerobic biodegradation mechansims) and unsubstantiated, particularly for the UWBZ where a pilot EBR test was not performed, and these TOR estimates ignore that fact that slow NAPL dissolution can ~~will~~ have a significant impact on biodegradation. Therefore, these time estimates appear to be unrealistic. For example, sensitivity analyses indicate that decreasing the biodegradation rate to 0.00038 d^{-1} (5-year half-life), which is similar to the maximum utilization rate for the UWBZ that AMEC cites in Table E-4.11 of their RD-RAWP report, increases the TOR by more than a factor of ten for the UWBZ (TOR > 130 years; Memorandum Table 6).

Commented [DJC3]: Bo, I tried to make this section less confusing by using your more simple first-order, equilibrium calcs

Commented [DE4]: How does this rate compare to other literature values?

Commented [DE5]: Dan didn't think the rates calculated for the LSZ from the pilot test that was done were reliable

Commented [DE6]: Should these be changed around, increasing the decay constant decreases the TOR?

Modeling was then performed for NAPL depletion using a rate-limited NAPL dissolution model [representative, site-specific first-order NAPL mass transfer rate of 0.05 d^{-1} in the LSZ; LNAPL mass transfer tests were not performed in the UWBZ) and a more comprehensive Monod kinetics model for biodegradation (using the site-specific, calibrated parameter values from the SEAM3D modeling effort; BEM, 2011). These same parameter values (with the exception of NAPL dissolution rate) are cited in Table E-4.11 of the ST012 RD-RAWP Work Plan (AMEC, 2014). However, as discussed in Section 4.5.6 of the RD-RAWP report, AMEC ~~apparently~~ increased the maximum utilization rates (Table E-4.11) by a factor of 10 for their EBR modeling and TOR estimates. For the volume-averaged model the calculated TOR with Monod kinetics ranged from 90 to 140 years in the UWBZ and 8 to 23 years in the LSZ (Memorandum Table 10). These estimates are based on site measured properties and calibration to site conditions. Sensitivity calculations indicate increasing the mass transfer coefficient by a factor of ten yields a slight decrease in the TOR, suggesting that ~~the groundwater is near equilibrium~~ slow dissolution from the NAPL does not significantly inhibit biodegradation in areas where the mass transfer rate is on the order of 0.05 d^{-1} and the hydrocarbon utilization rate is on the order of 10^{-3} d^{-1} (Table E-4.11 values). An order-of-magnitude decrease in the mass transfer coefficient (i.e., 0.005 d^{-1}) increased the TOR in the LSZ by a factor of four but yielded a marginal increase in the TOR in the UWBZ, suggesting biodegradation is the limiting process. Note that when the maximum hydrocarbon utilization rate is increased by a factor of ten (~ 0.01 d^{-1}), which is the rate AMEC used in their EBR modeling, the biodegradation rate is very sensitive to NAPL dissolution rates when the NAPL mass transfer rate is on the order of 0.05 d^{-1} or smaller. For example, with a 0.01 d^{-1} utilization rate the TOR in the UWBZ increases by a factor of two to three with a 0.005 d^{-1} LNAPL dissolution rate. Further, note that these volume-averaged results can be expected to underestimate TOR values because the box model assumes that (i) the porous media is homogeneous, (ii) the aqueous-phase (soil and water) concentrations are spatially uniform (i.e., well-mixed), and (iii) the NAPL residual saturation and associated NAPL mass transfer rates are spatially uniform. The AMEC EBR model also assumes homogenous soil properties within a specific water-bearing zone. In addition AMEC did not perform any EBR parameter sensitivity analyses, similar to those contained in the attached memorandum, that would allow critical review of their TOR estimates and EBR modeling approach. Actual conditions during EBR at the ST012 site will not be "well-mixed" (e.g., large variations in hydrocarbon and sulfate concentrations), the subsurface is heterogeneous (e.g., highly-variable hydraulic conductivity, soil grain size, biological populations, etc.), and NAPL saturations are highly variable (e.g., nonlinearly and inversely correlated with soil grain size). In other words, very small NAPL dissolution rates (e.g., much smaller than 0.05 d^{-1}) and rate-limited desorption of dissolved hydrocarbon mass from low-permeability zones (as observed in pump-and-treat systems) can be expected to extend remediation times beyond the TOR estimates determined using the volume-averaged model.

Commented [DE7]: Does this still use the rate constant that Amec used?

Commented [DJC8]: Bo, I wrote these 2 sentences based on my BoxModel spreadsheet. you should check

Based on the volume-averaged model and underlying assumptions, the concentration of sulfate-reducing bacteria grew to a stationary-phase range of 3 to 3.5 mg/L (biomass per bulk soil volume) in both zones, when growth occurred. The growth period was approximately 12 to 24 months in the LSZ. The growth period in the UWBZ was on the order of 35 to 40 years assuming a zero death rate. The UWBZ growth was slow and the results were very sensitive to the death rate as a result of the low utilization rate. These modeling results highlight the importance of quickly establishing and maintaining high biomass concentrations in order to optimize EBR. Therefore, AMEC's TOR estimates for EBR appear to also be optimistic due to the fact that they did not incorporate either biomass changes with time or their related effects on biodegradation rates (i.e, they assumed biodegradation would not be limited by biomass availability). Finally, the calculated TOR was not strongly influenced by the assumed initial biomass concentration (0.01 mg/L). In addition, initial sulfate concentrations exceeding 8,000 mg/L provided no improvement in the TOR.

Commented [DE9]: Suthersand et al. (2011) gives 2000 mg/l for sulfate no longer rate limiting

Based on the model and its output, study topics for the first phase of sulfate reduction at the site include:

1. Will engineered degradation rates yield attainment of remedial objectives in desired timeframes? The TOR estimates presented in this memorandum show that the EBR modeling by AMEC ignores critical NAPL mass-transfer and biodegradation (e.g., biomass changes) mechanisms and does not adequately evaluate the impacts of heterogeneities on EBR time frames.
2. Will the sulfate reducing bacteria (SRB) biomass grow as needed?
3. What is the optimal concentration for sulfate injection?
4. Will highly concentrated injections of sulfate be inhibitive to bacterial activity?
5. Will the injected sulfate become well distributed with respect to NAPL accumulations?
6. What is the lag time for SRB to acclimate to elevated sulfate concentrations (not included in the model)?
7. Inhibition by other degradation processes and nutrient availability are not included in the model, are these factors important?
8. Will hydrogen sulfide concentrations or other reaction products inhibit degradation or will subsurface conditions mitigate their buildup?
9. If/when sulfate is no longer limiting rates of degradation, what will limit the reaction and what degradation rates can be expected?
10. Is benzene slower to degrade than other aromatics, or faster, or average?
11. Will periodic sulfate injections or recirculation be necessary to sustain degradation rates?
12. How will the actual depletion of aromatic compounds from NAPL be assessed (i.e., robust NAPL sampling and measurement of hydrocarbon concentrations in NAPL samples are critical to demonstrating EBR performance)

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